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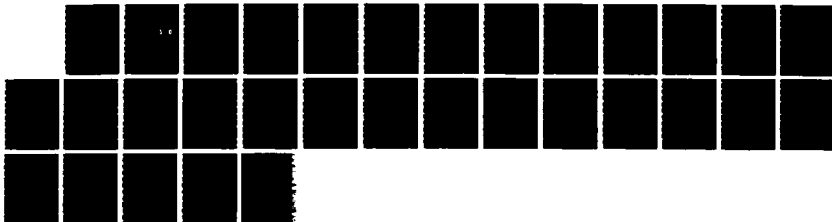
MULTIDISCIPLINARY APPROACH TO THE SCIENCE AND
TECHNOLOGY OF SUB-MICRON EL (U) MICHIGAN UNIV ANN
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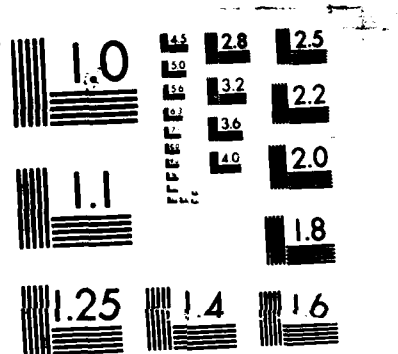
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MULTIDISCIPLINARY APPROACH TO THE SCIENCE AND
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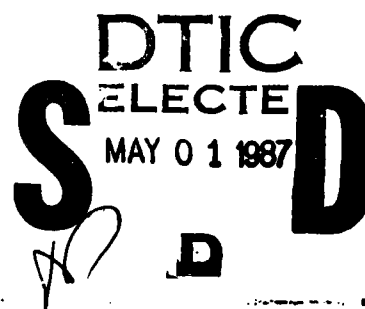
FINAL REPORT

AUTHOR (S)

Roy Clarke

DATE

3/11/87



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The University of Michigan
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The final report describes research in two related focal areas: i) Electronic properties and behavior of heterointerfaces including quantum well structures. ii) Interfacial pattern formation and the dynamics of diffusion on fractal matter. Members of the three subtasks identified in the proposal have contributed synergistically to these two areas and a summary of the progress on each topic follows. Electronic behavior of heterointerfaces--The many-body theory of the electron gas in restricted geometries has been studied by Dr. Sander and his group (Task 2). The density functional method was used to calculate the sub-band energies and densities for electrons in accumulation and inversion layers in GaAs-Ge heterojunctions. Two-dimensional charge				
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¹⁹ densities as high as 3×10^{12} electrons cm^{-2} could be obtained with GaAs doping densities on the order of $3 \times 10^{18} \text{ cm}^{-3}$. Many-body effects are shown to be particularly important for the (110) and (111) Ge surfaces although not as large as those in the MOS systems.

In a related experimental study by Dr. Merlin's group (Task 3) resonant impurity states have been identified for the first time in GaAs (Si-doped)- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum well structures using electronic Raman scattering techniques. These localized states are expected to strongly influence the transport properties of multiple quantum well (MQW) devices by serving as hot electron traps, perhaps leading to negative differential conductances. 1s-2s acceptor transitions have also been observed in Be-doped GaAs- Al_{1-x}As MQW's but the spectra are very complex.

In an extension of this work, an entirely new kind of superlattice has been fabricated by members of Task 3. This type of superlattice, which was designed to have "quasi-periodic" ordering, is expected to have very unusual properties, particularly in the tunneling behavior. There are potential technological applications in oscillator technology in this connection. Work is continuing on doped GaAs-AlAs quasi-periodic superlattices in collaboration with Professor Bhattacharya in the EE Department.

Other activities in the area of heterointerfaces include studies of the effects of paramagnetic impurities and structural disorder at the interface of mismatched Mo-Ni superlattices in Dr. Uher's group (Task 3). Also, investigations of metal-semiconductor contacts using gold dispersions on oxide supports such as MgO and TiO_2 have been made (Drs. Schwank and Fogler (Task 1)). In the latter project the presence of the metal is found to strongly influence the structural stability of the oxide support material indicating significant modification of the bonding properties at the interface. Pattern formation and kinetics of diffusion on fractals--The growth of ultra-small structures, including superlattices made by deposition methods such as MBE, is a process that generally proceeds far from thermodynamic equilibrium. In such cases (generally referred to as "disorderly growth") atomic arrangements may form which are quite unlike bulk equilibrium crystal structures. It is therefore important to understand the underlying mechanisms involved in such cases. Dr. Sander and his students (Task 2) have been studying disorderly growth processes mostly in the two-dimensional regime which is appropriate for modeling growth at interfaces and on surfaces.

A series of experiments have been carried out which model the process of disorderly growth via fluid flow. Also extensive use is made of numerical simulations to study the scaling properties of disorderly growth. Often such situations are found to be 'fractal'-like in nature. An important recent finding on this project is the identification of different types of growth (faceted, tip splitting, needle crystal and dendritic) depending on the degree of anisotropy present at the interface. Ballistic growth models have also been studied and these may be relevant to MBE growth far from equilibrium.

Dr. Kopelman (Task 2) has addressed the dynamics of diffusion controlled processes on the surface of fractal matter. The important issue here is the nature of charge carrier transport at interfaces, surfaces and in amorphous materials. Dr. Kopelman's group has been studying non-classical rate coefficients using super-computer simulations and exciton recombination reactions in real fractal systems such as polymeric glasses and porous membranes. New scaling laws have been proposed for chemical reactions and recombination kinetics in ultra-small fractal clusters.

Progress Report: "Multidisciplinary Approach to the Science and Technology of Sub-micron Electronics." 10/15/83--3/15/84.

CONTENTS: Overview
Summary of findings by each subtask
List of publications resulting from this grant
List of senior personnel and graduate students

Overview

In the initial phase of the project, the focus of the three subtasks of the program is to explore some very basic physical mechanisms in small clusters and thin films which are pertinent to sub-micron electronic device configurations.

Clearly several important interconnections between the findings of the various research tasks are already beginning to emerge. For example, the successful preparation of controlled sizes of gold particles in Task 1 is a necessary step towards testing the theoretical predictions on random aggregation and percolation that are coming out of Task 2. Likewise the interface characterizations of Kopelman's group, coupled with the theoretical studies of electron-electron interactions in heterostructures, provide important insights into the experimental results on localization and electronic structure in Task 3. These and other related findings will be pursued in more depth during the coming months. In the second year of funding we intend to extend the base of the program, which is rather fundamental in these initial stages, to give the supplementary work units described in our proposal a more central position. These include work on contacts for ultra-small devices (Elta and Hansell, Electrical and Computer Engineering) and computer architecture (Frieder and Holland, Computer Science and Engineering). The latter work is under consideration for funding by U.S. Army Electronic Devices Laboratory, Fort Monmouth (Contact: Ed Poindexter).

The unique expertise which characterizes the University of Michigan USER group makes us well placed to study both theoretical and experimental aspects from several different viewpoints. It is important, therefore, to have an organizational framework for the program which fully exploits this synergism. Accordingly, we have set up, with the help of University funds, a new research office (Ultra-small Structures Research Office). Overseeing the whole program is a faculty advisory committee composed of representatives from each of the subtasks and senior faculty from the Computer Science and Engineering, Electrical Engineering, and Chemistry departments. The main purpose here is to maintain good communications and cross-stimulation between the various groups. To further strengthen the multidisciplinary advantages of our program we are instituting a regular seminar symposium where each of the sub-tasks will present their results to the whole group. It is important that the graduate students associated with the projects will be actively involved in this process.



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We have identified and recruited six highly motivated graduate students who are now working as full-time research assistants in the program.

Below is a brief summary of the most important research results in each of the three subtasks.

TASK 1: PREPARATION AND CHARACTERIZATION OF ULTRASMALL METAL CLUSTERS

J. Schwank and H.S. Fogler

Great success has been achieved in the preparation of metallic microparticles within microemulsion systems. Microparticles of Au, Pt, Au-Ag, and Pt-Ru have been prepared using the microemulsion technique within the penta-ethylene glycol dodecyl ether (PEGDE)/Hexadecane/water system. Resultant particles are analyzed by transmission electron microscopy (TEM) and selective chemisorption to characterize particle size and composition, respectively. Catalytically active particles of uniform size ($30 \pm 5 \text{ \AA}$) and composition are produced by direct reduction of metal salts confined to the water cores of inverted micelles. The 'caging' effect of the inverted micelles ensures a narrow distribution of particle size, and a uniform composition. This exciting method for preparation of ultrasmall particles has potential applications in catalyst preparation, microelectronics, photographic systems and magnetic recording technology.

Besides the preliminary test of prototypes of ultrasmall metal clusters, we also focused our attention on support materials, in particular MgO and TiO₂. We studied the changes in BET surface area and porosity of these materials as a function of thermal pretreatment. Our findings lay the ground for the use of TiO₂ and MgO as substrates for small metal particles produced by the microemulsion technique.

TASK 2: COMPUTER SIMULATIONS AND THEORY OF LOCALIZATION

R. Kopelman and L. Sander

The progress in this area is directed towards the exploration of transport in restricted and random geometries and many-body effects in narrow layers.

R. Kopelman has pointed out that recent results of random walks on percolation clusters (the Alexander-Orbach hypothesis) could have important practical consequences: in particular, trapping and reactions of carriers (e.g., electrons, excitons) have an anomalous, universal behavior: chemical reactions slow down and trapping is non-exponential. A verification of the hypothesis in realistic cases is the subject of a preprint. Sander and a student, Z.H. Cheng, have very recently verified the chemical reaction behavior for random diffusion-limited aggregates on surfaces. This work, which is now being written up, may be relevant to catalysis, and predicts interesting electronic effects of random traps in a random environment.

A second preprint, by Sander and a student, J. Hautman, is a careful analysis of electron-electron interactions in inversion layers and heterostructures. It is shown that the standard theories overestimate these effects by, typically, 30-50%. This should have an impact on the theory of ultra-small devices.

Kopelman's group has made progress in characterizing film formation on a realistic rough interface. The goal of this project is to see to what extent simplified models (percolation, etc.) are relevant to real situations.

TASK 3: STRUCTURE AND ELECTRONIC BEHAVIOR OF SUPERLATTICES AND MULTIPLE HETEROSTRUCTURES

R. Clarke, R. Merlin, J. Potts and C. Uher

The goal of this task is to provide a better experimental understanding of the electronic structure and transport mechanisms of restricted geometry structures such as metallic and semiconducting heterostructures.

One set of experiments performed by Uher's group studies the in-plane resistivity in short-wavelength ($\lambda \leq 50\text{\AA}$) Ni/Mo superlattices. They observe a fascinating interplay between superconducting behavior (Mo) and magnetic effects (Ni) when the individual layers are very thin ($\leq 15\text{\AA}$). A very interesting observation is that the conduction electrons are localized for these small thicknesses. We have performed transport measurements down to $\sim 10\text{mK}$ in a dilution refrigerator. The localization is thought to arise from the random potential due to lattice mismatch at the Mo/Ni interface. Clarke's group has probed this disorder using X-ray diffuse scattering techniques. The observed behavior has important consequences for the nature of electron transport in ultra-small devices where random potentials may be unavoidable.

A second set of experiments, performed by Merlin and Potts' group, is investigating the electronic band structure of multiple quantum well structures based on $\text{GaAs-A}_x\text{Ga}_{1-x}\text{As}$. Donor states, formed by Si-doping are probed by resonant Raman scattering and are found to be hydrogenic in character. The observed $1S \rightarrow 2S$ transitions are associated with the donors near the center of the well. Broadening of the spectral lines reflects the spread of impurity levels induced by the confinement, transitions to higher lying levels, and donor-donor interactions. Related studies on GaAs and Fe/GaAs by Merlin's group have shown the existence of a two-dimensional electron layer due to the presence of a confining potential near the surface or at the metal/semiconductor interface. These preliminary results demonstrate the power of resonant light scattering techniques to probe the detailed nature of electronic states in quantum well devices.

Publications and Preprints Resulting from Funding Under
Grant ARO DAAG 29-83-K-0131

- 1) "Interplay of Superconductivity, Magnetism and Localization in Mo/Ni Superlattices," C. Uher, R. Clarke, G.-G. Zheng and I.K. Schuller, submitted to Physical Review Letters.
- 2) "Photoexcited Two-Dimensional Electron System at the Surface of Semi-Insulating GaAs", T.A. Perry, J.E. Potts, R. Merlin, G.A. Prinz and E.M. Swiggard, submitted to Physical Review Letters.
- 3) "Raman Scattering from Electrons Bound to Shallow Donors in GaAs- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ Quantum Well Structures," B.V. Shanabrook, J. Comas, T.A. Perry and R. Merlin, submitted to Physical Review B.
- 4) "Long Range Random Walk on Percolation Clusters," P. Argyrakis and R. Kopelman, accepted in Physical Review B.
- 5) "Non-local Exchange Correlation Energy in Quasi Two-dimensional Electron Layers," J. Hautman and L.M. Sander, submitted to Physical Review B.

Research personnel supported in part by ARO are underlined.

Research Personnel

Senior Investigators

G. Gamota	Professor of Physics and Director of Institute of Science and Technology
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R. Kopelman	Professor Chemistry
R.D. Merlin	Assistant Professor of Physics
J.E. Potts	Associate Professor of Natural Sciences
L.M. Sander	Professor of Physics
J.W. Schwank	Assistant Professor of Chemical Engineering
C. Uher	Associate Professor of Physics

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J. Hautman (Task 2)
T.A. Perry, M. Winokur, D. Morelli (Task 3)

PROGRESS REPORT

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8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED
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TASK 1: PREPARATION AND CHARACTERIZATION OF ULTRASMALL METAL CLUSTERS

J. Schwank and H.S. Fogler

Ultrasmall metal clusters supported on semiconducting or insulating substrates represent model systems for understanding the relationship between the structure, morphology surface chemistry and charge carrier transport of aggregated systems. A novel microemulsion technique is being used to prepare metal clusters with unprecedented narrow particle size distributions ($\pm 3\text{\AA}$). For example, uniform platinum particles of 30\AA , and gold particles up to 700\AA in size can be produced on TiO_2 and MgO using this technique. Elliptical gold colloids with silver in, or on, them have also been made in $700 \times 350\text{\AA}$ sizes.

The samples are subjected to a thorough multifaceted characterization procedure and in this phase of the project a high vacuum, recycle reactor has been constructed for this purpose. The system has a gas handling capability with provision for in-situ mass spectrometer analysis and simultaneous monitoring of electrical conductivity changes. This apparatus will facilitate an understanding of the electronic changes following gas adsorption, desorption and reaction on the ultrasmall metal clusters. The stability of dispersions of small gold clusters on TiO_2 as a function of thermal treatments has been studied. Adsorbate-adsorbate interactions in the CO adsorbate on such highly dispersed Au samples are then analyzed using various models. A preliminary report on this work is currently being prepared for publication.

TASK 2: COMPUTER SIMULATIONS AND THEORY OF LOCALIZATION

R. Kopelman and L. Sander

The single random walk simulations on percolation clusters discussed in the previous semi-annual report by Professor Kopelman's group have been extended to long-range random walks on percolation clusters. The hopping time is found to vary with distance and various functional forms have been simulated giving the exploration range (S_N , mean number of distinct sites visited after N steps), the mean-square displacement, etc. The results are consistent with the superuniversality conjecture. This supposes that chemical trapping or localization on random walk percolation clusters obeys a simple scaling behavior $S_N \sim N^{d_s/2}$, where $f = \frac{1}{2} d_s = \frac{2}{3}$.

Ensembles of reacting random walkers have also been simulated on fractal spaces. They support the scaling approach results, which is in marked contrast with classical chemical kinetics. For instance, for the recombination reaction $2A \rightarrow \text{products}$, it is found that the recombination rate is not proportional to n_A^2 (n_A being the density of A walkers) but rather to

n_A^x where $x = 1/f - 1$. As f usually varies between $\frac{1}{2}$ and 1, x lies between 2 and 3. For percolating clusters $x = 2.5$; $x = 2.45$ for a Sierpinski gasket (a model fractal lattice) and for a simple linear arrangement $x=3$. It is expected that these results will be of much importance for the motion and interaction of charges and excitons on submicron strands and aggregates. Professor Sander and his associates are carrying out further computer simulations which specifically address the universality features of random aggregates in order to determine whether new length scales are associated with the surfaces of such objects, and to see whether classical instability theory can shed more light on the growth of aggregates. A summary of their findings is included in the attached preprint.

A more immediately applicable study is described in a second preprint by Professor Sander: it shows how to explicitly and exactly treat certain finite size effects in photo diodes and his theory could lead to improvements in the efficiency of photodetectors.

TASK 3: STRUCTURE AND ELECTRONIC BEHAVIOR OF SUPERLATTICES AND MULTIPLE HETEROSTRUCTURES

R. Clarke, R. Merlin and C. Uher

The goal of this task is to provide a better experimental understanding of electronic transport mechanisms in ultrasmall layered structures such as metallic and semiconducting heterostructures. Work on the in-plane resistivity of short wavelength ($\lambda \leq 50\text{\AA}$) Ni/Mo superlattices is continuing and preparations are being made to investigate the unusual resistivity plateau observed at $T < 0.5\text{K}$ in the non-superconducting (ferromagnetic) samples $\lambda > 18\text{\AA}$. The dilution refrigerator necessary to achieve these temperatures is being fitted with a superconducting magnet in order to separate out magnetic effects from the influence of interface defects. The existence of the unexpected plateau, indicating a truncation of the localization behavior at very low temperatures, has been checked carefully by immersing samples inside the mixing chamber of the dilution refrigerator. Further modeling of the X-ray scattering data from real (i.e., imperfect) heterostructures has been carried out by Professor Clarke and colleagues using the Hendricks-Teller formulation.

Professor Merlin has recently identified transitions associated with resonant donor states in GaAs (Si-doped)- $\text{AP}_x\text{Ga}_{1-x}\text{As}$ multiple quantum well structures. These states derive from higher two-dimensional subbands. A report of these findings will be presented at the International Conference on Molecular Beam Epitaxy in San Francisco. (see attached preprint).

SUMMARY AND OVERVIEW

Important results on the mechanisms of charge transport and localization have been obtained from computer simulations and measurements on metallic superlattices. The findings are highly non-classical and represent a new insight into the treatment of the dynamics of inhomogeneously distributed matter. An interesting synergism is developing between the work on percolative systems and Dr. Frieder's project on ultrasmall computer architecture. The latter has recently been funded by EDTL, Fort Monmouth and now forms an integral part of our USER program. Professors Clarke and Uher visited EDTL (contact Dr. E. Poindexter) in June, 1984 in order to present an overview of the University of Michigan USER project.

PUBLICATIONS AND PREPRINTS RESULTING FROM FUNDING UNDER

GRANT ARO DAAG 29-83-K-0131

- 1) "Interplay of Superconductivity, Magnetism and Localization in Mo/Ni Superlattices", C. Uher, R. Clarke, G.-G. Zheng and I.K. Schuller, Phys. Rev. B30 453 (1984).
- 2) "Electronic Transport in Mo/Ni Superlattices", R. Clarke, D. Morelli, C. Uher, H. Homma and I.K. Schuller, Proceedings of the International Conference on Superlattices, Urbana, Aug, 1984. (to be published).
- 3) "Photoexcited Two-Dimensional Electron System at the Surface of Semi-insulating GaAs", T.A. Perry, J.E. Potts, R. Merlin, G.A. Prinz and E.M. Swiggard, Phys. Rev. B30, 15 July, 1984.
- 4) "Raman Scattering Studies of Donor Transitions in Semiconductor Quantum Well Structures", T.A. Perry, R. Merlin, B.V. Shanabrook and J. Comas, Proceedings of the International Conference on Molecular Beam Epitaxy, San Francisco, Aug, 1984.
- 5) "Exact Solution for the Peripheral Photoresponse of a p-n Junction", L.M. Sander, (submitted to Phys. Rev. B).
- 6) "Theory of Fractal Growth Processes", L.M. Sander, Proceedings of International Conference on Kinetics of Aggregation and Gelation, Atlanta, GA. April, 1984.
- 7) "Long-range Random Walk on Percolation Clusters", P. Argyrakis and R. Kopelman, Phys. Rev. B., Aug., 1984.
- 8) "Fractal Kinetics: Simulations and Experiments, L.W. Anacker and R. Kopelman, (submitted to J. Chem. Phys.).
- 9) "Non-local Exchange of Correlation Energy in Quasi Two-Dimensional Electron Layers," J. Hautman and L.M. Sander, (submitted to Phys. Rev. B).

Research personnel supported in part by ARO are underlined.

PROGRESS REPORT

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8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED
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TASK 1: PREPARATION AND CHARACTERIZATION OF ULTRASMALL METAL CLUSTERS

J. Schwank and H.S. Fogler

Monodisperse Pt particles have been prepared in a water/oil microemulsion system; particle size distributions were 1.8 ± 0.3 nm for a reaction time of 5 min., 1.9 ± 0.2 nm at 17 min., and 2.1 ± 0.2 nm at 40 min., respectively. All samples are stable in storage for at least three weeks. Research on composite metal colloids has been initiated. Gold-palladium, gold-platinum and gold-ruthenium composite particles are being produced in microemulsion, using hydrazine as a reducing agent. Gold and palladium are completely miscible. Gold and platinum form several compounds, while gold and ruthenium are immiscible. The effect of mutual solubility of the metals on the nature of the colloid formed is under investigation.

Progress has also been made in the characterization of gold particles supported on TiO_2 dielectric substrates. the gold particles are found to stabilize the TiO_2 surface against phase transitions up to very high temperatures. Infrared spectroscopic evidence has been found for an activation of the TiO_2 surface for adsorption of CO gas due to interaction with Au. Details of this work are reported in a paper presented at the AIChE annual meeting in November 1984 (copy attached).

TASK 2: COMPUTER SIMULATIONS AND THEORY OF LOCALIZATION

R. Kopelman and L. Sander

Models and simulations for recombination reactions on disordered media reported previously have been extended. The earlier work dealt with "homofusion" reactions ($A+A \rightarrow A$) that are appropriate for exciton recombination. An extension to "heterofusion" ($A+B \rightarrow 0$) has been accomplished; the results are relevant to electron-hole recombination, etc. In these cases the fluctuations are more severe and much longer times are needed to reach a steady state, with important implications for solid state and surface chemical reactions in the ultra-small scale regime. We have also added refinements to our investigations of random walkers with variable range hops. The results are in agreement with theoretical speculations and seem to support one model (Aharony-Stauffer), over an alternate model (Alexander-Orbach), irrespective of hopping range. These models aim to describe the dynamics of excitations in two-dimensional percolation clusters.

A second study in this sub-task relates to theoretical descriptions of ballistic aggregation, i.e., the microscopic growth properties of a stream of atoms or molecules impinging on a cold substrate. This would be the situation prevailing when, for example, one attempts to evaporate thin metal layers on a semiconductor at low temperature to prevent inter-diffusion. The problem is treated in terms of a mean-field marginal stability analysis. The formation of unusual surface structures, such as "fans" and columnar growth that are typically encountered under low-temperature substrate conditions, are found to

be a natural consequence of the anisotropy of the growth process. A number of geometrical factors of practical interest, such as the universal tilt angle of the columns relative to the surface, are derived from the theory. The work, described in an attached preprint, is relevant to experimental studies of ultra-high vacuum deposition which are presently underway in Task 3 of the USER project.

TASK 3: STRUCTURE AND ELECTRONIC BEHAVIOR OF SUPERLATTICES AND MULTIPLE HETEROSTRUCTURES

R. Clarke, R. Merlin and C. Uher

Our efforts in this period concentrated on Raman studies of antimonium-doped GaAs/(AlGa)As quantum-well structures doped with Si donors and Be acceptors. For the donor work, we were able to observe for the first time transitions involving resonant bound states. The impurity states that overlap with the continuum are unique to the quantum well structures. A paper describing our findings has been submitted for publication. Regarding acceptors, the work is at a preliminary stage. Data at high power densities reveal transitions between hole subband and, at low powers, structures that are associated with the impurities, likely the same transitions between resonant states is observed for donors.

Ultra-high vacuum instrumentation purchased with University funds to grow metal-semiconductor heterostructures by the Molecular Beam Epitaxy technique is presently being installed. The equipment will facilitate the growth of heterostructures which are complementary to the GaAs/(AlGa)As quantum well structures described above. Problems concerning the growth of metal-semiconductor composite heterostructures will be investigated including the fundamental behavior of transport in these systems in the region where the modulation spacing of layers is comparable to the electron quantum wavelength.

Publications resulting from funding under Grant ARO DAAG 29-83-K-0131 during the period 7/1/84-12/31/84:

1) "A comparative FTIR and Chemisorption Study of O₂ and CO Interactions with Highly Dispersed Gold.", A.G. Shastri, J.Y. Lee, A.K. Datye and J. Schwank, to be published in the Proceedings of the Annual Meeting of the American Institute of Chemical Engineers, San Francisco, 1984.

2) "Space Charge Layers in Semi-insulating GaAs: Photoexcited Two-dimensional Electron Systems", T.A. Perry, J.E. Potts, R. Merlin, G.A. Prinz and E.M. Swiggard, (submitted to Solid State Communications).

3) "Comment on Enhanced Raman Scattering from Adsorbates on Semiconductor Surfaces", J.E. Potts and R. Merlin, Surface Science 147, L617 (1984).

4) "Theory of Ballistic Aggregation", R. Ramanlal and L.M. Sander, submitted to Phys. Rev. Lett.).

Research personnel supported in part by ARO are underlined.

PROGRESS REPORT

TWENTY COPIES REQUIRED

1. ARO PROPOSAL NUMBER: 21069-EL
2. PERIOD COVERED BY REPORT: 1 January 1985 - 30 June 1985
3. TITLE OF PROPOSAL: Multidisciplinary Approach to the
Science & Technology of Sub-Micron
Electronics
4. CONTRACT OR GRANT NUMBER: DAAG29-83-K-0131
5. NAME OF INSTITUTION: University of Michigan
6. AUTHORS OF REPORT: _____ ROY CLARKE _____
7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP
DURING THIS REPORTING PERIOD, INCLUDING JOURNAL REFERENCES:

See list at end of report

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED
DURING THIS REPORTING PERIOD:

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J. Hautman, P. Garik (Task 2)
T. Perry, D. Gammon, R. Hockey,
J. Cohn (Task 3)

In this, the second year of the project, research has centered on two related focal areas:

- i) Electronic properties and behavior of heterointerfaces including quantum well structures.
- ii) Interfacial pattern formation and the dynamics of diffusion on fractal matter.

Members of the three subtasks identified in the proposal have contributed synergistically to these two areas and a summary of the progress on each topic follows.

Electronic behavior of heterointerfaces

The many-body theory of the electron gas in restricted geometries has been studied by Dr. Sander and his group (Task 2). The density functional method was used to calculate the sub-band energies and densities for electrons in accumulation and inversion layers in GaAs-Ge heterojunctions. Two-dimensional charge densities as high as 3×10^{12} electrons cm^{-2} could be obtained with GaAs doping densities on the order of 3×10^{18} cm^{-3} . Many-body effects are shown to be particularly important for the (110) and (111) Ge surfaces although not as large as those in the MOS systems.

In a related experimental study by Dr. Merlin's group (Task 3) resonant impurity states have been identified for the first time in GaAs (Si-doped)- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum well structures using electronic Raman scattering techniques. These localized states are expected to strongly influence the transport properties of multiple quantum well (MQW) devices by serving as hot electron traps, perhaps leading to negative differential conductances. 1s-2s acceptor transitions have also been observed in Be-doped GaAs- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ MQW's but the spectra are very complex.

In an extension of this work, an entirely new kind of superlattice has been fabricated by members of Task 3 (see enclosed preprint). This type of superlattice, which was designed to have "quasi-periodic" ordering, is expected to have very unusual properties, particularly in the tunneling behavior. There are potential technological applications in oscillator technology in this connection. Work is continuing on doped GaAs-AlAs quasi-periodic superlattices in collaboration with Professor Bhattacharya in the EE Department.

Other activities in the area of heterointerfaces include studies of the effects of paramagnetic impurities and structural disorder at the interface of mismatched Mo-Ni superlattices in Dr. Uher's group (Task 3). Also, investigations of metal-semiconductor contacts using gold dispersions on oxide supports such as MgO and TiO_2 are continuing (Drs. Schwank and Fogler (Task 1)). In the latter project the presence of the metal is found to strongly influence the structural stability of the oxide support material indicating significant modification of the bonding properties at the interface.

Pattern formation and kinetics of diffusion on fractals

The growth of ultra-small structures, including superlattices made by deposition methods such as MBE, is a process that generally proceeds far from thermodynamic equilibrium. In such cases (generally referred to as "disorderly growth") atomic arrangements may form which are quite unlike bulk equilibrium crystal structures. It is therefore important to understand the underlying mechanisms involved in such cases. Dr. Sander and his students (Task 2) have been studying disorderly growth processes mostly in the two-dimensional regime which is appropriate for modeling growth at interfaces and on surfaces.

One of the attached preprints includes an account of an experiment which models the process of disorderly growth via fluid flow. Also extensive use is made of numerical simulations to study the scaling properties of disorderly growth. Often such situations are found to be 'fractal'-like in nature. An important recent finding in this project is the identification of different types of growth (faceted, tip splitting, needle crystal and dendritic) depending on the degree of anisotropy present at the interface.

Dr. Kopelman (Task 2) is addressing the dynamics of diffusion controlled processes on the surface of fractal matter. The important issue here is the nature of charge carrier transport at interfaces, surfaces and in amorphous materials. Dr. Kopelman's group has been studying non-classical rate coefficients using super-computer simulations and exciton recombination reactions in real fractal systems such as polymeric glasses and porous membranes.

Contact with Army laboratory personnel

During the year we have received visits from Dr. E. Poindexter and Dr. J. Iafrate of EDTL, Fort Monmouth. Dr. Iafrate gave a seminar in the Physics Department on ultra-small electronics research. Dr. Strosio visited members of the USER team on April 17, 1985 and Dr. C. Boghosian and Dr. Poindexter attended the USER Symposium at the University of Michigan on May 17, 1985. One of our team, Dr. Merlin, has become a consultant to EDTL, considerably strengthening our interactions with this laboratory. Dr. Robin Ball (Cambridge University) is a visiting research scientist at the University of Michigan during August and September with funding provided by the ARO London office.

Publications resulting from funding under Grant ARO DAAG 29-83-K-0131 during the period 1/1/85 - 6/30/85:

- 1) "Sub-band Structure of n-type Accumulation and Inversion Layers in GaAs-Ge Heterojunctions", J. Hautman and L.M. Sander submitted to Physical Review Letters.
- 2) "Observation of Resonant Impurity States in Semiconductor Quantum Well Structures", T.A. Perry, R. Merlin, B.V. Shanabrook and J. Comas, Physical Review Letters 54, 2623 (1985).

- 3) "Quasi-periodic GaAs-AlAs Heterostructures", R. Merlin, K. Bajema, R. Clarke, F.-Y. Juang and P.K. Bhattacharya, submitted to Phys. Rev. Letters.
- 4) "Influence of Noble Metal Particles on Semiconducting and Insulating Oxide Materials", J. Schwank, A.G. Shastri and J.Y. Lee, ACS Symposium Series (in press).
- 5) "Experimental Demonstration of the Role of Anisotropy in Interfacial Pattern Formation", E. Ben-Jacob, R. Godbey, N. Goldenfeld, J. Koplik, H. Levine, T. Mueller and L.M. Sander, submitted to Physical Review Letters.
- 6) "Growth by Particle Aggregation", L.M. Sander, to be published in the proceedings of the NATO Advanced Study Institute, Geilo, Norway (April, 1985).
- 7) "Diffusion-controlled Reaction Kinetics on Fractal and Euclidian Lattices: Transient and Steady State Annihilation", L.W. Anacker, R.P. Parson and R. Kopelman, J. Phys. Chem. (in press).
- 8) "Anisotropic Growth of Diffusion-limited Aggregates", P. Garik, submitted to Phys. Rev. B.
- 9) "Electronic Transport in Mo/Ni Superlattices", R. Clarke, D.T. Morelli, C. Uher, H. Homma and I.K. Schuller, Superlattices and Microstructures I, 125 (1985).

Names of personnel supported in part by this grant underlined.

PROGRESS REPORT

TITLE: COPIES REQUIRED

1. APO FEDERAL NUMBER: 01089-EL

2. PERIOD COVERED BY REPORT: 1 July 1987 - 31 December 1987

3. TITLE OF PROJECT: Submicron Planar Approach to the
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4. DATE OF REPORT: 14-02-88-01-001

5. APO INSTITUTION: University of Michigan

6. AUTHOR OF REPORT: ROY CLARKE

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PROGRAM. ADDITIONAL REFERENCES:

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1. TITLE OF PROJECT: Submicron Planar Approach to the
Science & Technology of Sub-micron
Electronics

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S. Russell, J. Cohn, F. Lamelas	(Task 3)

Progress is described in the two thrust areas of electronic behavior of heterostructures and the kinetics of diffusion on fractals.

Heterostructures

As mentioned in the previous report (1/1/85-6/30/85), a new class of heterostructure has been developed at the University of Michigan as a result of a collaboration between the solid state physics group (Merlin, Clarke) and the electronic materials group in EE (Bhattacharya). The new superlattice is based on a quasiperiodic MBE sequence of GaAs and AlAs layers. Exploration of the unusual structure and electronic properties is continuing. Photoluminescence spectra show several unexpected features and the photoelectric response is unusually large. A high-resolution synchrotron X-ray study (Clarke) of the quasiperiodic superlattice reveals that the structural coherence of the superlattice is very much better than one would at first expect since the individual layer thicknesses are only accurate to ~5% because of the inevitable instabilities in the MBE source flux. The ability to achieve extremely sharp spectral response from a multilayer system may have useful technological implications for improved X-ray and UV mirrors. Other interesting potential applications are suggested by the strong non-linearity of the system.

A study of the first bi-structural superlattice, made from Ru and Ir layers, was presented by our USER group at the recent conference on Heterostructures and Interfaces (Materials Research Society Annual Meeting, Boston, December, 1985). The major finding was that the superlattice became isostructural when the Ir layers were very thin (<30Å). The role of interface strains and interdiffusion in stabilizing short wavelength bistructural superlattices was investigated.

Other work in this area concerned the interface between Ru and Au clusters and dielectrics such as MgO and SiO₂ (Schwank and Fogler). In this project it was found that large Au particles exhibited random alignment on the MgO surface whereas Au particles of less than 50Å diameter take up an 110/111 epitaxial registry. Again, the presence of interfacial strain is of paramount importance in determining the deposition of metal layers on an unlike substrate.

Pattern Formation and Fractal Kinetics

The main effort in this area has been in exploring and understanding the relationship between morphology, pattern formation and microstructure in growth processes far from equilibrium. Our experimental and theoretical studies have recently led to an explanation for the crossover from disorderly (fractal) growth to dendritic growth. It appears that anisotropy is the key factor which leads to long range crystalline order at high driving force.

In parallel with these studies on fractal growth Dr. Kopelman's group has carried out a series of Monte-Carlo simulations on the kinetics of diffusion in fractal matter. Most recently this group has formulated a new set of kinetic laws relating to exciton and electron-hole recombination processes in restricted channels and fractal networks. The channel dimensions considered were 30-6000Å in width.

Contact with Army Laboratory Personnel

Dr. Merlin has visited EDTL, Fort Monmouth, twice during the present reporting period in order to discuss common interests with Dr. Poindexter's group and to present seminars on current topics in semiconductor physics. Dr. Poindexter visited R. Clarke at the University of Michigan and R. Clarke attended the meeting on the Future of Microstructures Technology at Seabrook Island, NC. At this meeting R. Clarke had extensive discussions with Dr. M. Strosio, Dr. J. Hurt (ARO) and Dr. J. Iafrate (EDTL) regarding new developments in the U of M ultra-small electronics research group.

Publications Resulting from funding under Grant ARO DAAG 29-83-K-0131 during the period 7/1/85-12/31/85

1. "Fibonacci GaAs-AlAs Superlattices", R. Clarke, R. Merlin, K. Bajema, F.-Y Juang and P.K. Bhattacharya, Proc. Int. Conf. on Phonon Physics, 1985 (in press).
2. "Quasiperiodic GaAs-AlAs Heterostructures", R. Merlin, K. Bajema, R. Clarke, F.-Y Juang and P.K. Bhattacharya, Phys. Rev. Lett 55, 1768 (1985).
3. "X-ray and Transport Studies of Ruthenium-Iridium Bicrystal Superlattices," in Heterostructures and Interfaces, Proc. Materials Research Society, 1986 (in press).
4. "Morphology and Microstructure in Electrochemical Deposition of Zinc," D. Grier, E. Ben-Jacob, R. Clarke, and L.M. Sander, Phys. Rev. Lett. (in press).
5. "Experimental Demonstration of the Role of Anisotropy in Interfacial Pattern Formation", E. Ben-Jacob, R. Godbey, N.D. Goldenfeld, J. Koplik, H. Levine, T. Mueller and L.M. Sander, Phys. Rev. Lett. 55, 1315 (1985).
6. "Fractal and Fractal-like Reaction Kinetics," L.W. Anacker and R. Kopelman, Proc. Mater. Res. Soc., 1985 (in press).
7. "Fractal Aspects of Heterogeneous Chemical Reactions", P. Argyrakis and R. Kopelman, in Adv. in Chemical Reaction Dynamics, Eds. P.M. Rentzopis and C. Capellos (D. Reidel, Dordrecht, 1985).
8. "Microstructure of Bi-metallic Ru-Cu/SiO₂ Catalysts: A Chemisorption and Analytical Electron Microscope Study", A.G. Shastri and J. Schwank, J. Catalysis (in press).
9. "A Convergent Beam Electron Diffraction Study of Bi-metallic Ru-Au/MgO Catalysts", A.G. Shastri and J. Schwank, J. Catalysis (in press).

ROY CLARKE

See list at end of report

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A. McKiernan, F. Lamelas,
J. Cohn.

Progress is described in each of the three task areas;

Task 1: Preparation and characterization of Ultrasmall Metal Clusters

In the past six months, the work on the multifaceted characterization of bimetallic ultrasmall metal clusters was continued with special emphasis on chemisorption, and high-resolution transmission electron microscopy coupled with energy dispersive X-ray analysis and electron microdiffraction. We discovered that the relative interdispersion of two metals in small (<4 nm) bimetallic clusters can be quite different depending on the preparation conditions of the clusters. Comparing Ru-Au and Ru-Cu particles of 1 to 4 nm in diameter, we found that Au tends to form islands on the surface of Ru, while Cu tends to decorate the Ru surface atomically. This difference in interdispersion results in drastic differences in the adsorption behavior towards molecular hydrogen. On Ru-Au, sufficiently large Ru ensembles remain intact and accessible to the adsorbing H_2 , so that the H_2 chemisorption behavior of Ru is not significantly influenced by the presence of the Au. In the case of Ru-Cu, however, the Cu atoms disrupt the surface of Ru to such an extent that the dissociative adsorption of molecular H_2 is strongly suppressed.

Task 2: Pattern Formation and Fractal Kinetics

In this area the work has been mainly concerned with the relationship between pattern formation and fractal growth. We have been mostly working on electrodeposition of zinc and have been developing a theory to describe the crossover from fractal pattern formation to dendritic growth. A theory has also been developed to describe the formation of thin films via vapor deposition. This is related to experimental work carried out in Task 3 on heterostructures. We find that a model of ballistic aggregation can be used successfully to describe the appearance of columnar microstructure in experiments on thin film growth. This work is described in more detail in a preprint listed below.

There have been some other interesting developments in the area of restricted channels and networks. Our newly-discovered kinetics laws for exciton recombination have been extended to the case of electron-hole recombination in ultrasmall channels and disordered media. This leads to the unexpected possibility of segregated electrons and holes under steady-state conditions (i.e., steady formation of electron-hole pairs via radiation and steady recombination). The Monte-Carlo simulations involve large ensembles of interacting random walkers and were carried out, in part, on supercomputers (Cyber 205), utilizing our specially designed algorithms. Furthermore, we investigated the detailed statistical properties (variance, higher moments) of random walks on random aggregates and on percolation networks, resulting in novel relations. These results are relevant to experiments which are underway in our laboratory on electronic transport and electron-hole recombination in narrow channels and disordered networks.

Task 3: Structural and Electronic Behavior of Superlattices and Multiple Heterostructures

Two main developments have been pursued: experiments on new quasiperiodic superlattices and studies of quantum-well structures.

In the quasiperiodic (Fibonacci) superlattices we have obtained synchrotron X-ray data; the results show excellent agreement with the calculated profile for an ideal structure. This indicates that quasiperiodic ordering is strongly insensitive to random fluctuations in growth parameters. Raman scattering by longitudinal acoustic phonons in Fibonacci superlattices shows a weighted density of states revealing the rich structure of the phonon spectrum. A large number of gaps were experimentally observed, all related through powers of the golden mean.

Preliminary optical data on these superlattices show a rich excitonic structure that correlate with calculated positions of principal gaps. The properties of excitons in these structures have not as yet been studied theoretically. They could be very different from "normal" excitons as the effective mass is not defined in this case.

Contact with Army Laboratory Personnel

During this reporting period we received a visit from Dr. M. Stroschio of ARO in connection with our URI proposal. Dr. Gary Vezzoli of USAAMCCOM-SMCAR Dover, NJ, also visited in connection with the possibility of depositing magnetic monolayers by MBE.

Publications resulting from funding under Grant ARO #DAAG29-83-K-0131 during the period 1/1/86-6/30/86

1. "Influence of Noble Metal Particles on Semiconducting and Insulating Oxide Materials", ACS Symposium Series, Vol. 198, Ch. 18, American Chemical Society, Washington, DC (1986). J. Schwank, A.G. Shastri and J.Y. Lee.
2. "The Influence of Hydrozine Reduction on Metal Dispersion and Support Morphology in Bimetallic Ru-Au/MgO Catalysts", J. Catalysis 98, 191 (1986). A.G. Shastri and J. Schwank.
3. "Electron Microscopy and Krypton Adsorption Characterization of High-Purity MgO Powder", J. Mater. Res. 1, 114 (1986). M. Bretz, A.G. Shastri and J. Schwank.
4. "Theory of Ballistic Aggregation and Deposition", L.M. Sander, Multiple Scattering of Waves in Random Media and Random Rough Surfaces, eds. V.V. Varadan and V.K. Varadan, Technomic, 1986.
5. "Steady State Chemical Kinetics on Fractals: Segregation of Reactants", L.W. Anacker and R. Kopelman, submitted to Phys. Rev. Letters.

6. "Morphology and Microstructure in Electrochemical Deposition of Zinc", Phys. Rev. Lett. 56, 1264 (1986).
7. "Fibonacci GaAs-AlAs Superlattices", R. Merlin, K. Bajema and R. Clarke, in Phonon Physics, ed. J. Kollar (World Scientific, Singapore, 1985), p. 541.
8. "Synchrotron X-ray Study of a Fibonacci Superlattice", J. Todd, R. Merlin, R. Clarke, J. Axe and K.M. Mohanty, Phys. Rev. Lett. 57, 1157 (1986).

(Underlined: Personnel supported by this grant.)

PROGRESS REPORT

TWENTY COPIES REQUIRED

1. ARO PROPOSAL NUMBER: 21069-EL
2. PERIOD COVERED BY REPORT: 1 July 1986 - 31 December 1986
3. TITLE OF PROPOSAL: Multidisciplinary Approach to the
Science & Technology of Sub-Micron
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4. CONTRACT OR GRANT NUMBER: DAAG29-83-K-0131
5. NAME OF INSTITUTION: University of Michigan
6. AUTHORS OF REPORT: _____ ROY CLARKE _____
7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP
DURING THIS REPORTING PERIOD, INCLUDING JOURNAL REFERENCES:

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8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED
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PROGRESS IS DESCRIBED IN EACH OF THE THREE TASK AREAS:

Task 1: Preparation and Characterization of Ultrasmall Metal Clusters

Ultrasmall metal particles supported on high surface area oxide substrates were investigated by a combination of chemical and physical probes with special emphasis on gas chemisorption and analytical electron microscopy. Particles containing bulk immiscible metal components such as Ru and Au were characterized by electron microdiffraction. One of the key questions pursued was how the preparative conditions influenced the composition and structure of the bimetallic particles. One of the objectives was to explore whether the structure of small bimetallic particles in a size range of 3-5 nm can be explained by atomic ordering or by random adsorption of one metal component on top of the other. Our results are in favor of a random adsorption model where one metal component decorates the surface of a small particle of the other metal. The details of preparation, however, dictate the relative degree of interdispersion and island size on the surface of these "bimetallic" particles.

Metal particles larger than about 10 nm showed random alignment with respect to crystalline substrates such as MgO. In the case of small Ru-Au particles (<5 nm in diameter) containing a gold core and exhibiting surface decoration by Ru, the (110) zone axis of Au was found to be parallel to the (111) zone axis of MgO. Small (<5 nm) bimetallic particles containing a Ru core with Au surface decoration were aligned with the (0001) zone axis of Ru parallel to the (111) zone axis of MgO.

The influence of the preparative conditions on bimetallic Ru-Cu particle formation was studied by temperature programmed reduction (TPR). The TPR profiles showed a simultaneous reduction of ruthenium and copper precursors even though the two constituent metals, Ru and Cu give in the case of monometallic preparations reduction peaks which differ by 150°C. The precursor compounds interact during the stages of preparation and removal of solvent, resulting in the formation of bimetallic aggregates during reduction. The stability of these bimetallic aggregates was found to be strongly dependent on the nature of the substrate; the most stable bimetallic particles were obtained on SiO₂, while Al₂O₃ and MgO supported particles were found to be more easily separated into monometallic particles of Ru and Cu.

Task 2: Pattern Formation and Fractal Kinetics

The question whether electrons and holes in very low-dimensional and disordered geometries may segregate, i.e., polarize macroscopically, has been further studied. Several quantitative criteria have been established for the analyses of the Monte-Carlo simulation data: 1. Chi-square tests; 2. Pair correlation functions; 3. Effective macroscopic charge dipoles. The most intriguing result so far is the significant polarization in strictly one-dimensional systems, resulting in very anomalous rules of recombination. Experimentally we have made much progress in the preparation of nanometer wires. Cylindrical wires, six microns long and with controlled radii from 8 to 500 nanometers, have been prepared, using a molecular exciton conductor. The very thin wires (below 20 nm) showed the theoretically (and

simulationally) expected one-dimensional recombination characteristics while the thicker wires showed the classical (3-dimensional) behavior. The preparation of 5 nanometer wires, as well as similar wires made of polymeric electron-conductors and semiconductors, is in progress. It appears that the wire cross-sections can be reduced well into the subnanometer domain.

Task 3: Structural and Electronic Behavior of Superlattices and Multiple Heterostructures

The research in this area has focussed on artificial quasiperiodic superlattices made from GaAs, AlAs and $\text{Ga}_x\text{Al}_{1-x}\text{As}$.

In one study, the optical absorption spectrum revealed a series of anomalies which correspond to the gaps in the electronic band structure. The unusual structure of these heterostructures, which is neither periodic nor random, is predicted theoretically to give rise to a hierarchy of gaps of widely differing magnitudes. Our optical measurements show that this unusual feature is not smeared out by fluctuations or imperfections in the superlattice.

An X-ray study of the structure also reveals that the unusual quasiperiodic structure is not very sensitive to imperfections. A summary of this work was recently published in Physical Review Letters. The finding that quasiperiodic behavior is not susceptible to fluctuations and imperfections is important because it implies that stable electronic and optical devices which may eventually be based on this new kind of structure, will be very robust and easier to fabricate than periodic multiple quantum well structures. In the latter materials, the properties are critically dependent on the thicknesses of individual wells.

Contact with Army Laboratory Personnel

During the reporting period we received a visit from Drs. E. Poindexter and J. Kohn of U.S. Army Electronic Devices and Technology Laboratories, Fort Monmouth (October 14-16, 1986). Discussions were held with all the USER faculty and with members of the Department of Electrical Engineering and Computer Science's Solid State Electronics Laboratory.

Publications Resulting from Funding under Grant ARO #DAAG29-83-K-0131 during the period 7/1/86 - 12/31/86

1. "Synchrotron X-ray Study of a Fibonacci Superlattice", J. Todd, R. Merlin, Roy Clarke, K.M. Mohanty and J.D. Axe, Phys. Rev. Lett. 57, 1157 (1986).
2. "Steady-State Chemical Kinetics on Fractals: Segregation of Reactants", L.W. Anacker and R. Kopelman, Phys. Rev. Lett. (in press).
3. "Reaction Dynamics in Low-Dimensional Systems", R. Kopelman, Proceedings of Conference on Disordered Systems, Bar Ilan, Jan 1987 (Proc. Roy. Soc., in press).

4. "The Microstructure of Bimetallic Ru-Cu/SiO₂ Catalysts: A Chemisorption and Analytical Electron Microscopy Study", A.G. Shastri, J. Schwank, and S. Galvagno, J. Catalysis, 100, 446 (1986).
5. "Characterization of MgO by Krypton Adsorption and Electron Microscopy", A.G. Shastri, J. Schwank and M. Bretz, World Congress, Chem. Eng. Tokyo. 1986, Vol. 1 270-3 (1986).
6. "Microstructure of Small Bimetallic Particles", A.G. Shastri and J. Schwank, in Microbeam Analysis 1986, eds. A.D. Romig, Jr. and W.F. Chambers (San Francisco Press, San Francisco, 1986) p. 623.

(Underlined supported by this grant)

END

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